SINTERING STUDY OF Mag-Al SPINEL SYNTHESIZED VIA COMBUSTION SYNTHESIS USING GLYCINE AS FUEL

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National Institute of Technology

Rourkela

CERTIFICATE

This is to certify that this thesis entitled**, "SINTERING STUDY OF Mag-Al SPINEL SYNTHESIZED VIA COMBUSTION SYNTHESIS USING GLYCINE AS FUEL" s**ubmitted by Mr. **KUNDAN PASWAN (Roll no.107CR034)** in partial fulfillment for the requirements for the award of Bachelor of Technology Degree in Ceramic Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Date: 16h May 2011

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16th May 2011 ***KUNDAN PASWAN***

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Abstract

The present work deals with the processing and sintering of phase pure Mag–Al spinel by auto-combustion process. Magnesium and aluminum nitrates have been used as the oxidizers and glycine as the fuel. Addition of glycine to the mixture of magnesium and aluminium nitrates results in a series of redox reactions to form a complex which subsequently crystallizes to form spinel at a lower temperature. Mag-Al spinel has been synthesized by varying metal to glycine ratio as 1:0.5, 1:1 and 1:2 and its effect on the spinel formation was studied. Variation of calcination temperature was done from 500^0 C to 1000^0C for 1 hour and 2 hours and their XRD analysis were performed to identify the exact starting temperature for obtaining phase pure spinel. The phase pure Mag-Al spinel was formed at 700 °C, when using metal to glycine ratio as 1:2. However, the phase pure Mag-Al spinel formation took place at higher temperature in case of other metal to glycine ratios. Bulk density was achieved in the range 3.135 – 3.34. Apparent porosity in the range of (0 – 6.64) % was achieved.

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Magnesium aluminate spinel is an advanced ceramic material possessing useful mechanical properties even at extreme temperatures hence is an invaluable material for high temperature application. Mag-Al spinel is a highly refactory material for its high melting point. Superior strength at ambient and elevated temperatures, superior corrosion, erosion, abrasion resistance and thermal spalling resistance are few of its remarkable properties which makes it an excellent refractory material. Due to above reasons it is used for application in side-walls and the bottom of steel teeming ladles, burning and transition zones of cement rotary kilns etc [1, 2]. It is used as major component in an alumina rich or magnesia rich matrix, according to its environmental condition of the application zones. Hence Magnesia or alumina rich spinel composition is important for application point of view. Being an important refractory material it may also be used in advanced application like high-temp arc-enclosing envelops, humidity and infrared sensors, transparent windows, domes and armour material [3].

Ultrafine homogeneous powder of single phase spinel can be used for the low temperature densification .combustion synthesis process have been found suitable for synthesizing powders for advanced application [4] .Ultrafine oxide ceramic powders of Al2O3, ZrO2, BaTiO3, LaCrO3, and Y2O3– ZrO2 has been produced by combustion synthesis [4-6]utilizing the exothermic redox reaction between an oxidizer and a fuel. The fuels are source of C and H and liberate heat as well as helps in Formation of complexes with the metal ions facilitating homogeneous mixing of the cations in solution [4]. Bhaduri et al [5-6] prepared both stoichiometric and non-stoichiometric Mag-AL spinel by combustion synthesis using urea as fuel and metal nitrates as oxidizers.

This work deals with the processing and sintering of phase pure Mag-Al spinel synthesized by auto-combustion process. Magnesium and aluminium nitrates have been used as the oxidizers and glycine as the fuel. Addition of glycine to the mixture of magnesium and aluminium nitrates results in a series of redox reactions to form a glycine - nitrate complex which subsequently crystallizes into spinel at a lower temperature. Results on the phase evolution and powder sinterability have been reported. A probable mechanism for low-temperature densification has also been suggested.

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

2.1 SPINEL:

Naturally occurring spinels are common high temperature minerals found in metamorophic rocks. It may also be present as non metallic inclusions in steel. It is one of the end members of its group minerals having general compositions AB_2O_4 where A is divalent ion like Mg, Fe, Mn and Zn and B is trivalent cation like Al^{3+}, Fe^{3+}.

2.2 SPINEL STRUCTURE:

The spinel group of minerals have the general formula AB_2O_4 where A is divalent (+2) cation and B is (+3) cation. The space group of spinel is Fd3m (227) with number of tetrahedral ‘a’ and octahedral d sites filled are 8 and 16 respectively [7]. Divalent sites are located on ‘a’ tetrahedral sites and the tetravalent cations are located on octahedral sites are on‘d’ sites. Generally, Spinels are denoted by formula AB_2O_4 and inverse spinels are denoted by $B(AB)O_4$. The intermediate cation distribution has formula $(A_{1-x}B_x)\ [B_{2-x}A_x]O_4$, where x is a inversion parameters having value range lies between $0 \leq x \leq 1$[8,9,10].

2.3 NORMAL AND INVERSE SPINELS:

In spinel the octahedral can be filled with B (trivalent) atoms and the tetrahedral with (divalent) atoms as no of octahedral are twice than tetrahedral and spinel has AB_2O_4 as formula. We can't reverse the roles of A and B and fill all the sites. Generally, most spinels lie between two end states. In the "normal spinel" structure, all the divalent cations are located on tetrahedral 'a' sites, while all trivalent cations are exclusively on octahedral'd' [11] sites. Generally, Spinels are denoted by formula AB_2O_4 and inverse spinels are denoted by $B(AB)O_4$.[13,14]. Spinel and chromite are normal spinels, magnetite is an inverse spinel [12]. The intermediate cation distribution has formula $(A_{1-x}B_x)[B_{2-x}A_x]O_4$, where x is a inversion parameters having value range lies between $0 \leq x \leq 1$.

2.4 IMPORTANCE OF MAGNESIUM ALUMINATE SPINEL:

Mag-Al spinel ceramic is useful for refractory as well as structural applications at elevated temperatures due to its high melting point, excellent mechanical strength and impressive chemical resistance. The most Stable compound present is $MgO\text{-}Al_2O_3$ system. It is chemically compatible with alumina, zirconia and mullite, hence spinel is good phase for ceramic matrix composite [15]. The major application areas of spinel refractory are burning zones of cement rotary kilns [1], sidewalls and bottom of steel teeming ladles and checker work of glass tank furnace generators as it is resistant to corrosion by slag. Alumina rich or magnesia rich matrix is suitable for spinel, depending upon the temperature and environment zone. Thus Mg rich and Al rich are very significant for use in refractory applications.

Compounds having Spinel structures are used for electrochemical uses, electrical applications. They are also used in semiconductor devices for semi conduction like in solar cell and also used in the biological applications.

2.5 PHASE DIAGRAM OF MgO-Al_2O_3

The binary phase of MgO and Al_2O_3 are shown in diagram. The melting point of magnesia is 2800^{o}C and alumina is 2020^{o}C as shown in diagram. At 50:50 molar compositions of MgO and Al_2O_3 the spinel phase formation occurs. Thus the spinel formed is a eutectic compound having congruent melting nature. Melting point of spinel is around 2135^{o}C. The spinel divides the whole system into two independent eutectic systems are MgO-$MgAl_2O_4$ and $MgAl_2O_4$-Al_2O_3 are present in spinel as shown in the diagram. So if a stoichiometric proportion of MgO and Al_2O_3 is taken, heated and cooled down slowly then at eutectic point, it gets converted to pure spinel

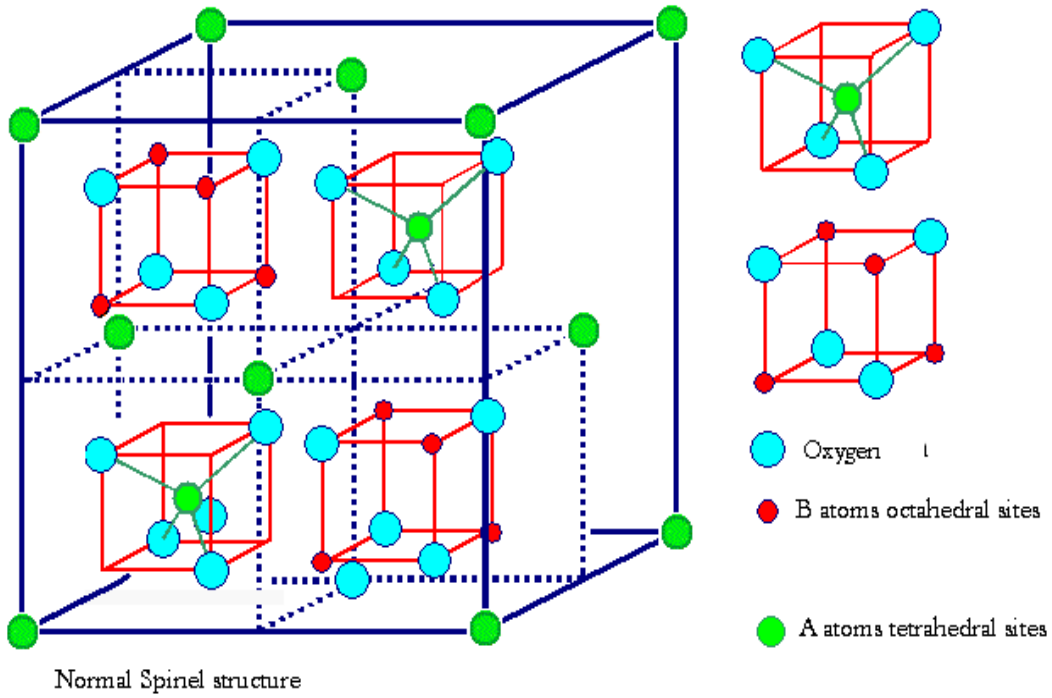

Figure 2.1: *structure of spinel*

The $MgO.Al_2O_3$ system is interesting to the refractory technologists, because spinel $MgO.Al_2O_3$ itself is a refractory and no liquid formation takes place with any mixture of pure magnesia and alumina at any temperatures below 1900 ^{o}C. Chesters and Parmelee showed that the reaction between equimolecular amounts of magnesia and alumina results in a substantial reaction-expansion [16]. This composition or one higher in magnesia composition can be made to produce steel-tight basic linings.

2.6 PREPARATION METHODS FOR SPINELS:

The methods of fabrication of spinel refractory has been known since 1905 [17] and the phase diagram of MgO-Al_2O_3 binary system has been well established since 1916. But still spinel did not get much of commercial success till mid-eighties mainly due to complexity in process parameters. Spinel formation from its constituent oxides (Al_2O_3 and MgO) is associated with 5-7% volume expansion, which hinders the densification process and does not allow the material to densify in the same firing schedule [18]. Hence a two-stage firing process was employed. The first step was to complete the spinel formation by getting the precursors calcined at an intermediate calcination temperature, and the second one to densify the formed spinel (1600^{o}-1800^{o}C). It is reported that the formation of spinel from magnesia and alumina does not produce dense product in a single stage firing, due to the volume expansion associated with it [19]. Hence the general practice is to complete the spinellisation process first and then crushing, milling, reshaping and sintering the spinel to achieve desired properties in the second-stage firing. Methods of preparing dense spinel products have improved considerably with progress of time. Various authors/ researchers have reported the preparation of spinel by different routes. The limiting factors for spinel preparation are the requirements regarding purity of the raw materials, their reactivity, intermediate calcination temperature, higher sintering temperature etc. Earlier many synthesis routes for spinel preparation have been implemented such as co-precipitation [20], combustion synthesis [21], etc. No doubt these methods have their advantages No doubt these methods have their advantages. These wet chemical routes reduce the formation/crystallization temperature of Mag-Al spinel to somewhat around 700°C. Even they help producing nano-powders. And this high surface area to volume ratio of ceramic sol makes

the powder sinter-active and hence high sinterability at lower temperatures is obtained. But the real challenge in synthesizing nano-structured powders using wet chemical routes is to control and engineer the physical properties of the starting materials as they affect the properties of the final products. To point out some disadvantages- in co-precipitation method usually Al/Mg-nitrate/ chloride salts are used. Repeated washing is required to remove the anions, which may alter the stoichiometric composition. Moreover, washing is a tedious and time consuming process. And regarding the combustion synthesis and sol-gel process- they involve chemicals that are sensitive to environment. Also, the reproducibility of the properties in the end products through these wet chemical routes is somewhat difficult to attain. However from industrial point of view, cost effective and less complicated techniques are required for large-scale application. In this context, solid-state reaction route is still the conventional and most feasible route in bulk production. However, the limitation is that it requires high calcination temperature and high sintering temperature. But to counter that there are mineralizers such as AlF_3, V_2O_5, Y_2O_3, NaCl, $MgCl_2$ etc. which promotes spinel formation at reduced calcination temperature and densification. Many schools have been studying on processing parameters and characterization of spinel and its composites, both stoichiometric and non-stoichiometric [22]. Literature shows that purer raw materials led to end products of better refractoriness and reactivity of starting materials largely influences both spinellisation reaction and densification of the spinel [23, 24]. In another work, it has been reported that fineness of the precursors attained by milling also plays a significant role in reactivity of starting materials. Generally oxide ceramics by themselves do not exhibit properties suitable to be used in desirable application areas. However through multiphase ceramic materials there is a possibility of developing microstructure through which the properties can be tailor made to handle desirable service environment. Generally,

MgO-rich spinel has been found to have better density and grain morphology than Al_2O_3 rich spinel. From earlier works, it can be said that incorporation of spinel particles of specific amount and particle size into magnesia refractories lead to the enhancement of mechanical properties of Mag-Al refractories.

Different types of method can be used for the production of single phase spinel powders for example flames spray pyrolysis et al [24], precipitation from organo-metallic [24][25], gelation and precipitation from an inorganic salt solutions[19], etc. But all the processes mentioned above include high temperature calcination step crystallization. Moreover, the processing of high density stoichiometric single phase magnesium aluminate spinel is rather difficult. Generally spinel of high density is prepared either by using high sintering temperature and use of oxygen atmosphere [26] or by using costly and specialized techniques like hot pressing [26], hot isostatic pressing [27] and cold isostatic process followed by sintering [28]

CHAPTER 3

OBJECTIVE OF THE PROJECT

OBJECTIVES

- To synthesize phase pure Mag-Al spinel at low temperature.
- Observe the change in Mag-Al spinel phase formation temperature with variation in metal: glycine ratio and calcination time.
- Study of apparent porosity and bulk density of Mag-Al spinel synthesized via combustion synthesis route using glycine as fuel.

CHAPTER 4

EXPERIMENTAL WORK

4. EXPERIMENTAL WORK:

4.1 SYNTHESIS OF Mag-Al SPINEL

4.1.1 RAW MATERIALS USED ARE:

- Magnesium nitrate hex-hydrate AR (LOBE CHEMIE PVT LTD.)
- Aluminum nitrate Nona-hydrate GR (LOBE CHEMIE PVT LTD.)
- Glycine acid (FISCHER SCIENTIFIC)
- 4% Poly vinyl alcohol

4.1.2 STOCK SOLUTION PREPARATION:

- 64.1 gm of $Mg(NO_3)_2.6H_2O$ was taken in 500 ml. of deionized water and dissolved by stirring
- 187.56 gm of $Al(NO_3)_3.9H_2O$ was taken in 500 ml. of deionized water and dissolved by stirring
- The above two solutions were mixed in a 2L. beaker and labeled as stock solution

Three different compositions was prepared by varying the metal: glycine ratios as 1: 0.5, 1: 1 & 1: 2

Composition 1: metal: glycine (fuel) = 1: 0.5; i.e. 11.25 g of glycine was used

Composition 2: metal: glycine (fuel) = 1: 1; i.e. 22.50 g of glycine was used

Composition 3: metal: glycine (fuel) = 1: 2; i.e. 45 g of glycine was used

4.1.3 COMBUSTION SYNTHESIS:

A. Composition 1

100 ml. of stock solution was taken in a 250 ml. beaker and 11.25 gm. of glycine as a fuel was added, a magnetic needle (for stirring) was put into the beaker. The beaker was placed on a hot plate (spinot) & both stirring and heating were done simultaneously. The heating regulator was kept between 4 & 5. The stirring regulator was also kept between 4 & 5 and after continued heating for 2-3 hours, the solution converted to gel like liquid and finally combustion took place leaving behind a black mass. After cooling, the black mass was collected in a plastic pouch and named black mass 1(BM1).

B. Composition 2

The above process was repeated by taking 22.50 gm. of glycine as a fuel. Finally combustion took place leaving behind a black mass. After cooling, the black mass was collected in a plastic pouch and named black mass 2(BM2).

C. Composition 3

The above process was repeated by taking 45 gm. of glycine as a fuel. Finally combustion took place leaving behind a black mass. After cooling, the black mass was collected in a plastic pouch and named black mass 3(BM3).

4.2 GENERAL CHARACTERIZATION

4.2.1 DIFFERENTIAL SCANNING CALORIMERTRY TEST

The three samples having varied metal to glycine ratio were characterized by DSC-TG (NETZS, GERMANY) at constant heating rate of 10°Cmin^{-1} in the temperature range of 30°C to 1000°C. Data was collected and graphs were plotted.

4.2.2 CALCINATION AT VARIOUS TEMPERATURES

Small amount of all the three samples (BM1, BM2&BM3) were taken in three different clean and dry alumina crucibles & put in furnace (BYSAKH) and calcined at various temperatures (400°C-1000°C) for different time period (1 and 2 hours) at heating rate of (3-5)°C/minute.

4.3 XRD ANALYSIS

After calcination X-Ray Diffraction was performed using Philips X-Ray diffractometer PW 1730 with nickel filtered Cu K_α radiation (λ=1.5406A^0) at 40 kV and 30mA. The scanning rate was set to 0.04°sec^{-1} and scanned continuously in the range of 15° to 60°C

4.4 PELLETIZATION

After the XRD analysis, the powders having metal to glycine ratio 1:2 and calcined at 700^{0}C, 800^{0}C & 900^{0}C for 2 hours were selected for circular and rectangular pellet preparation. The selected calcined powders were mixed with 4vol% PVA, an organic binder and ground with the help of a mortar and pestle. The three different powders were weighed differently and uniaxially pressed (CARVER, USA) at 3.5 tons with 90 sec. dwelling time.

4.5 SINTERING

The sintering was carried out in a chamber furnace at a maximum temperature of 1550°C. The heating rate in the furnace was 3°C /minute up to 1000° C with an intermediate soaking time of 1 hour at 550°C and 2°C/minute after 1000°C up to 1550°C. The samples were held for 2 hours at 1550°C.

4.6 APPARENT POROSITY AND BULK DENSITY CALCULATION

The bulk density and apparent porosity of the sintered pellets were determined by Archimedes principle using water. Dry Weight is measured and then the pellets were kept in distilled water and then vacuuming is done in place of boiling for about 45 min-1 hr. After that suspended weight is measured using apparatus in which pellet is suspended in water and weight is measured. After taking suspended weight, soaked weight is taken. Hence the dry weight, soaked weight and suspended weight were measured. The bulk density and apparent porosity were calculated by the formulas:

$$Bulk\ density = \frac{Dry\ wt.}{Soaked\ wt. - Suspended\ wt.}$$

$$Apparent\ porosity = \frac{Soaked\ wt. - Dry\ wt.}{Soaked\ wt. - Suspended\ wt.} * 100$$

CHAPTER 5

RESULTS AND DISCUSSION

5.1 DIFFERENTIAL SCANNING CALORIMETRY AND (DSC-TG) THERMOGRAVIMETRY

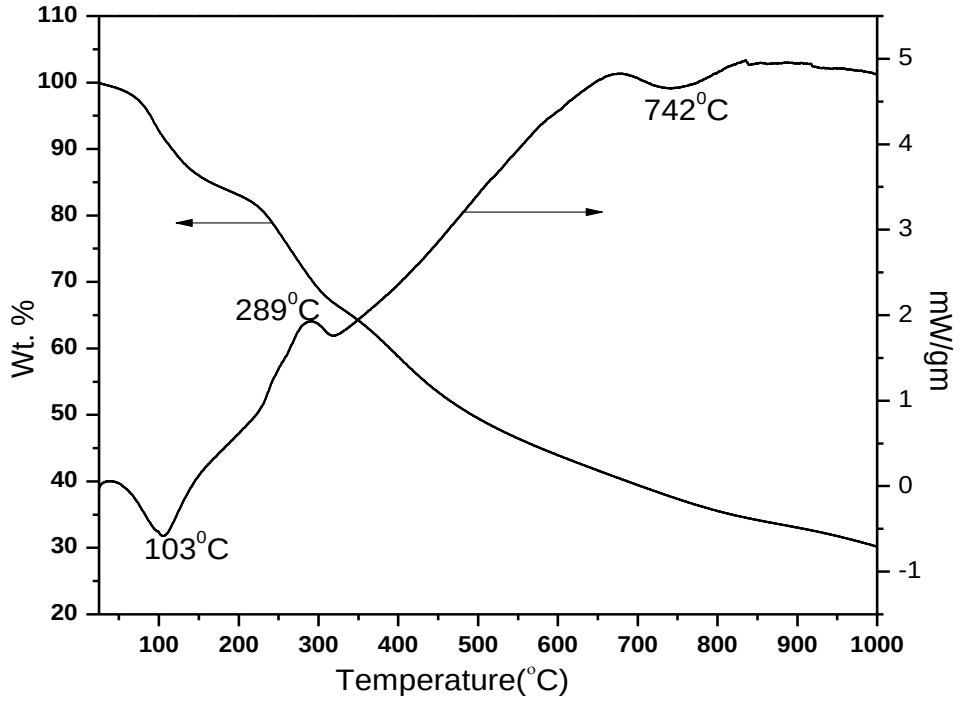

Figure5.1.a: *TG-DSC curves of the sample (metal*: *glycine ratio=1:0.5) synthesized via auto-ignition process*

It has been observed that at 103°C there is loss of physically bonded water. At 289°C, there is indication of burn out of residual organic phases. At 742°C there could be formation of spinel phase. There is gradual loss of weight up to 1000°C which indicates that there is huge amount of organic volatile materials present in the samples. These may be due to presence of glycine. The weight loss may also be due to decomposition of nitrates present in the samples.

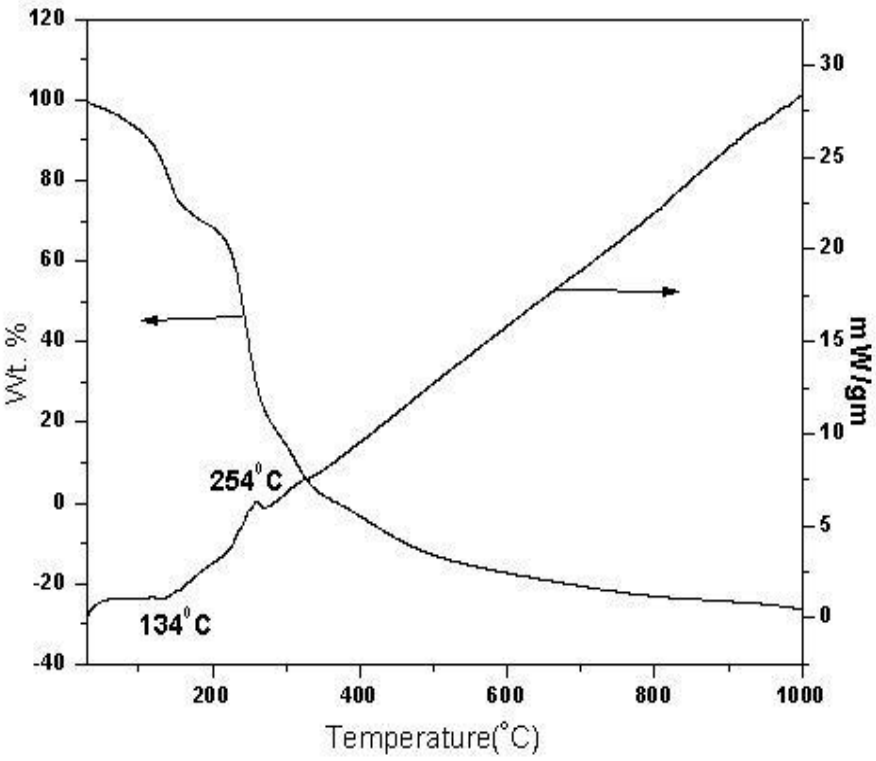

Figure5.1.b: TG-DSC curves of the sample (metal-glycine ratio=1:2) synthesized via auto-ignition process

It has been observed that at 134^{o}C there is loss of physically bonded water. There is indication of burn out of residual organic phases like previous graphs. There is no indication of formation of spinel phase. There is gradual loss of weight up to 1000^{o}C which indicates that there is huge amount of organic volatile materials present in the samples. These may be due to presence of glycine. The weight loss may also be due to decomposition of nitrates present in the samples.

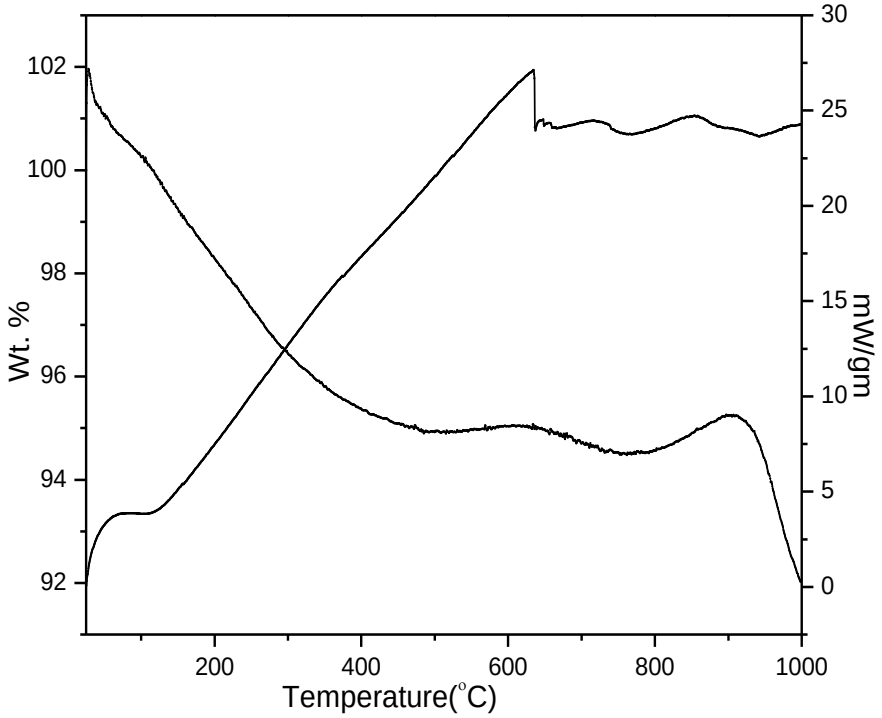

Figure5.1.c: *TG-DSC curves of the sample (metal-glycine ratio=1:1) synthesized via auto-ignition process.*

It has been observed that at 124^{o}C there is loss of physically bonded water. There is indication of burn out of residual organic phases like previous graphs. There is no indication of formation of spinel phase. There is gradual loss of weight up to 1000^{o}C which indicates that there is huge amount of organic volatile materials present in the samples. These may be due to presence of glycine. The weight loss may also be due to decomposition of nitrates present in the samples.

5.2 X-RAY DIFFRACTION

5.2.1 XRD pattern comparison at various temperatures when metal: fuel ratio of the sample is 1: 0.5 and calcined for1 hour.

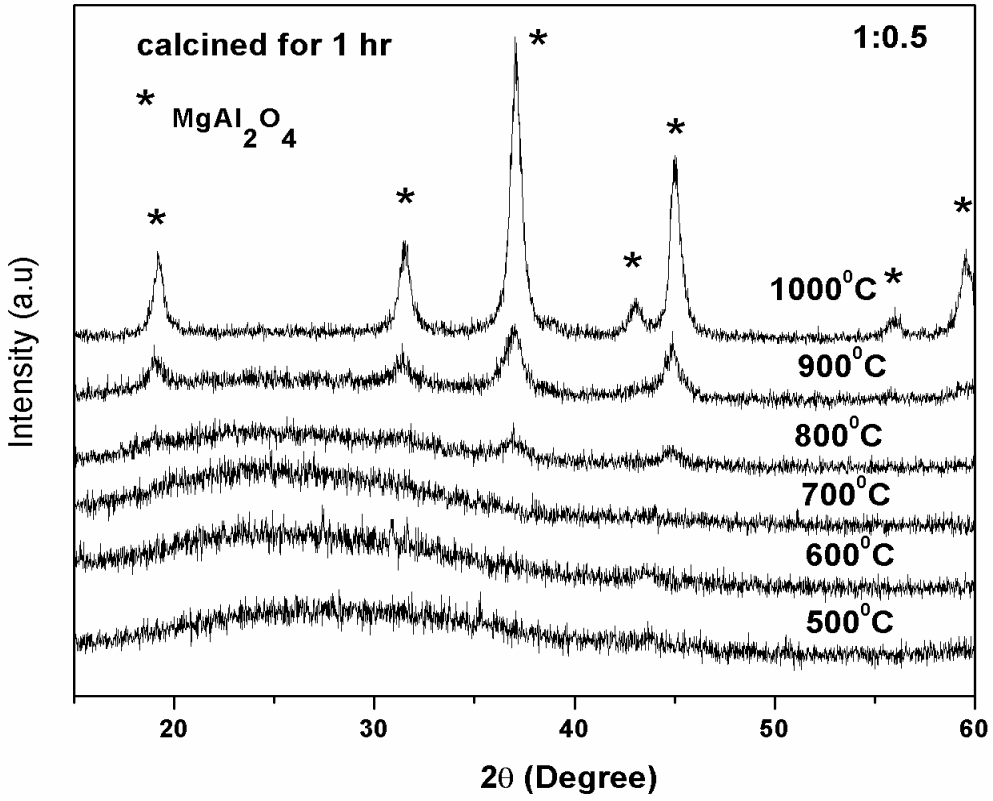

FIGURE 5.2.1: *XRD patterns of the powders having metal: glycine ratio 1:0.5 and calcined at various temperatures for 1 hour.*

It has been observed that at 500°C, 600°C, 700°C and at 800°C the sample is totally amorphous there is no trace of mag-Al spinel. At 900°C there is formation of Mag-Al spinel phase. With increasing temperature the intensity of the crystalline peaks increased. At 1000°C there is again sharp indication of spinel phase formation. So it can be concluded that spinel formation can take place only at and above 900°C.

5.2.2 XRD PATTERN comparison at various temperatures when metal: fuel ratio of the sample is 1: 0.5 and calcined for 2 hours

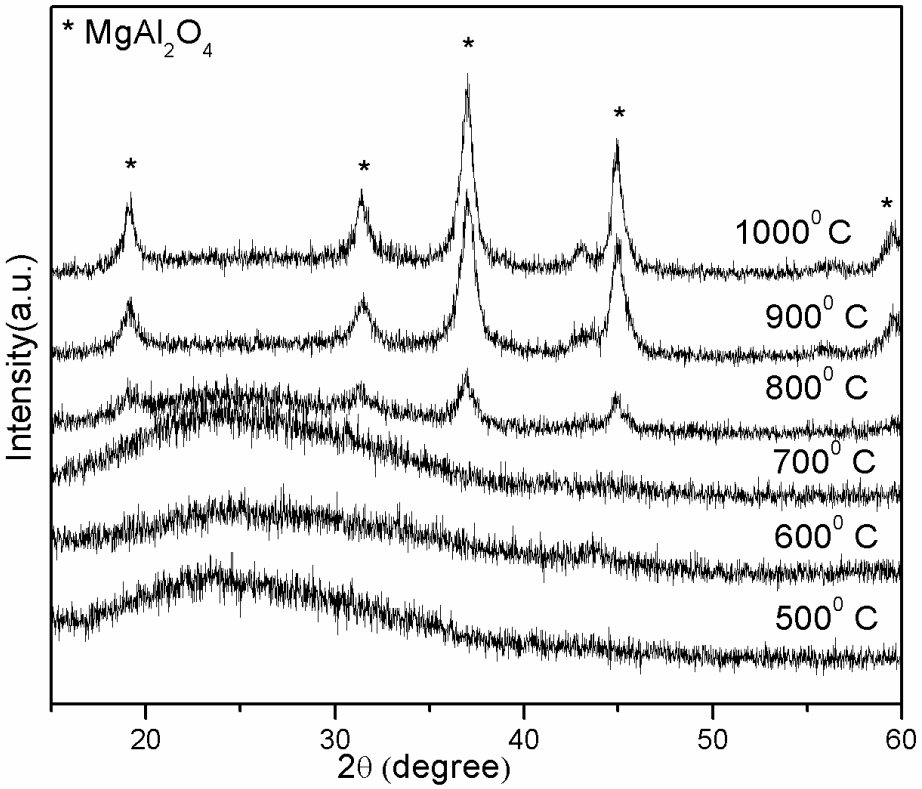

FIGURE 5.1.2: *XRD patterns of the powders having metal: glycine ratio 1:0.5 and calcined at various temperatures for 2 hours.*

It has been observed that at 500^{o}C, 600^{o}C and at 700^{o}C the sample is totally amorphous there is no trace of mag-Al spinel. At 800^{o}C there is formation of Mag-Al spinel phase. With increasing temperature the intensity of the crystalline peaks increased. At 900^{o}C there is again sharp indication of spinel phase formation. Again at 1000^{o}C there is again sharp indication of spinel phase formation. So it can be concluded that spinel formation can take place only at and above 800^{o}C.

5.2.3 XRD analysis comparison at various temperatures when metal: fuel ratio of the sample is 1: 1 and calcined for 1hour.

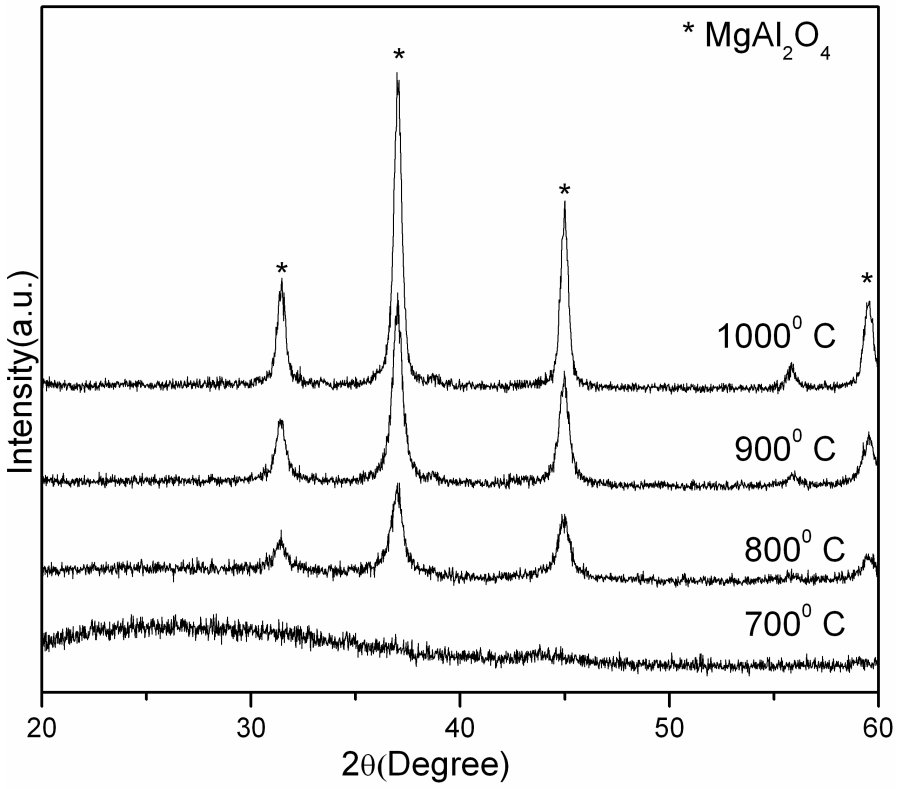

FIGURE 5.2.3: *XRD patterns of the powders having metal: glycine ratio 1:1 and calcined at various temperatures for 1 hour*.

It has been observed that at 700^{o}C the sample is totally amorphous there is no trace of Mag-Al spinel. At 800^{o}C there is sharp formation of Mag-Al spinel phase. With increasing temperature the intensity of the crystalline peaks increased. At 900^{o}C there is again sharp indication of spinel phase formation. Again at 1000^{o}C there is again sharp indication of spinel phase formation. So it can be concluded that spinel formation can take place only at and above 800^{o}C.

5.2.4 XRD analysis comparison at various temperatures when metal: fuel ratio of the sample is 1: 1 and calcined for 2hours

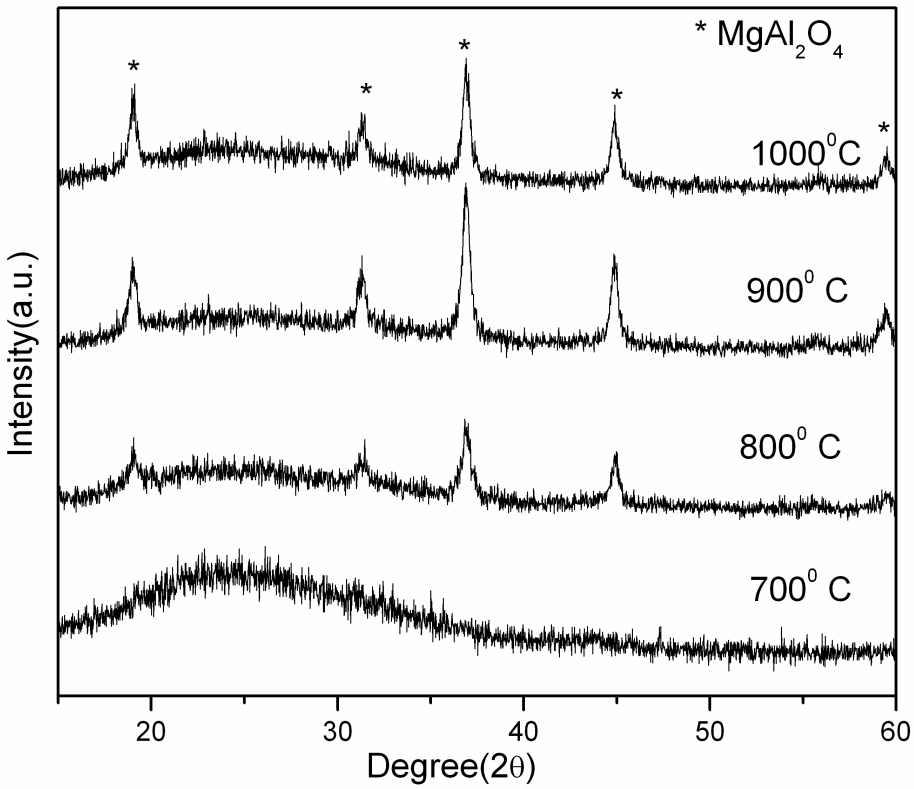

Figure 5.2.4: *XRD patterns of the powders having metal: glycine ratio 1:1 and calcined at various temperatures for2 hours.*

It has been observed that at 700^{o}C the sample is totally amorphous there is no trace of mag-Al spinel. At 800^{o}C there is sharp formation of Mag-Al spinel phase. With increasing temperature the intensity of the crystalline peaks increased. At 900^{o}C there is again sharp indication of spinel phase formation. Again at 1000^{o}C there is again sharp indication of spinel phase formation. So it can be concluded that spinel formation can take place only at and above 800^{o}C.

5.2.5 XRD analysis comparison at various temperatures when metal: fuel ratio of the sample is 1: 2 and calcined for 1hour.

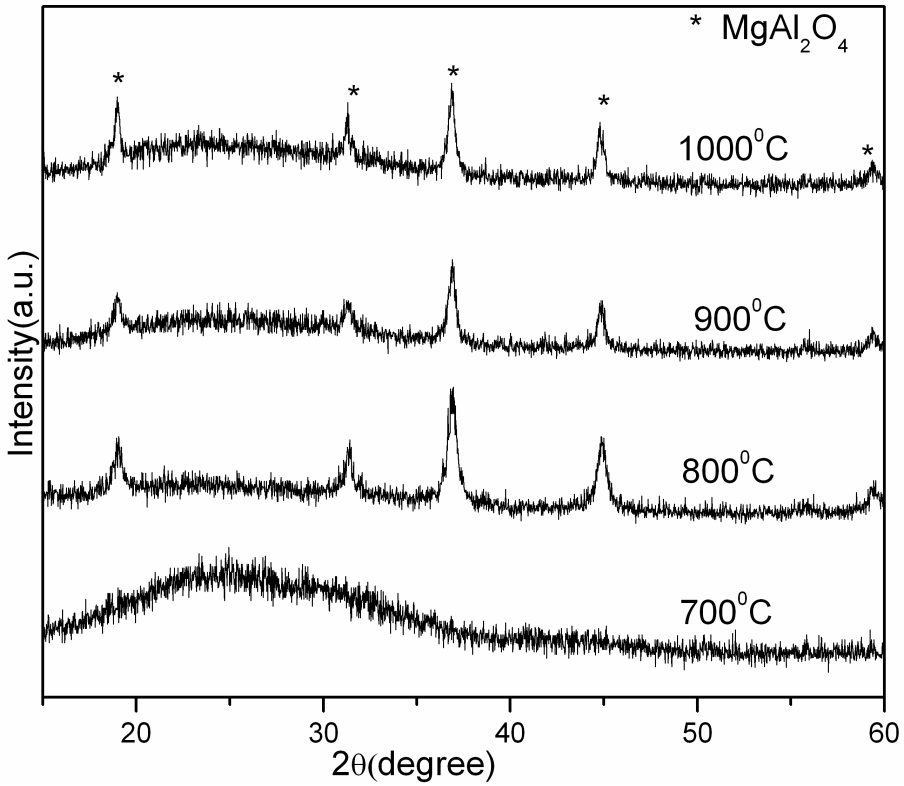

Figure 5.2.5: *XRD patterns of the powders having metal: glycine ratio 1:2 and calcined at various temperatures for 1 hour.*

It has been observed that at 700^{o}C the sample is totally amorphous there is no trace of mag-Al spinel. At 800^{o}C there is sharp formation of Mag-Al spinel phase. With increasing temperature the intensity of the crystalline peaks increased. At 900^{o}C there is again sharp indication of spinel phase formation. Again at 1000^{o}C there is again sharp indication of spinel phase formation. So it can be concluded that spinel formation can take place only at and above 800^{o}C.

5.2.6 XRD analysis comparison at various temperatures when metal: fuel ratio of the sample is 1: 2 and calcined for 2hours.

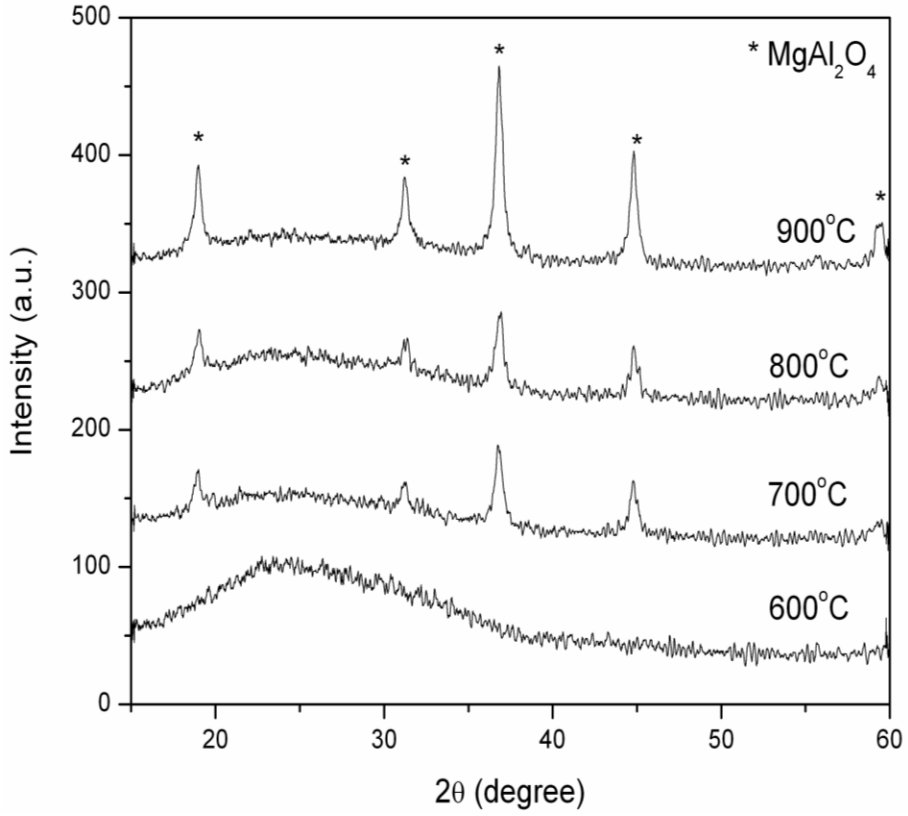

Figure 5.2.6: *XRD patterns of the powders having metal: glycine ratio 1:2 and calcined at various temperatures for2 hours.*

It has been observed that at 600°C the sample is totally amorphous there is no trace of mag-Al spinel. At 700°C there is sharp formation of Mag-Al spinel phase. With increasing temperature the intensity of the crystalline peaks decreased. It may be due to faulty batch preparation or may be due to some unknown reaction which leads to decomposition of Mag-Al phase at 900°C there is again sharp indication of spinel phase formation. So it can be concluded that spinel formation can take place only at and above 700°C.

5.3 APPARENT POROSITY AND BULK DENSITY TABLE:

The following table shows the apparent porosity and bulk density of sintered pellets.

SL NO.	SAMPLE NAME	DRY WT.	SOAKED WT.	SUSPENDED WT.	A.P(%)	B.D(g/CC)
1	72MA4500	0.4171	0.4254	0.3005	6.64	3.34
2	72MA4500	0.4155	0.4235	0.2910	6.03	3.135
3	72MA4500	0.4094	0.4094	0.2826	0	3.22
4	72MA4500	0.3835	0.3840	0.2653	0.42	3.23
5	82MA4500	0.3004	0.3015	0.2077	1.17	3.2
6	82MA4500	0.2965	0.2965	0.2054	0	3.25
7	92MA4500	0.3084	0.3092	0.2135	0.83	3.22

Figure 5.3 *AP & BD of samples (a)* **72MA4500**: *sample calcined at 700°c with metal: glycine ratio as 1:2 (b)* **82MA4500**: *sample calcined at 800°c with metal: glycine ratio as 1:2 (c)* **92MA4500**: *sample calcined at 900°c with metal: glycine ratio as 1:2*

The bulk density and apparent porosity measurement shows that there is very less amount of porosity present in the samples. In some cases there is no porosity observed. But the density of pure spinel phase is 3.58 gm/cc. But in the samples the measured bulk density is less than that value. As porosity is less as well as bulk density is also less than the 3.58 gm/Cc so it can be concluded that some closed pores are present in the samples due to which samples shows less density than ideal one.

CHAPTER 6

CONCLUSIONS

6. CONCLUSIONS

Spinel was formed at low temperature (700^0c) via auto-ignition/combustion synthesis process using metal: glycine ratio as 1: 2. Bulk density was achieved in the range 3.135 – 3.34 gm/cc. Apparent porosity in the range (0 – 6.64) % was achieved. It has been observed that with increase in glycine content the spinel formation temperature is decreased. The sintered samples show closed porosity after sintering. The samples show no porosity and in some cases maximum 6.5% open porosity in samples. The deviation from ideal bulk density in the samples is due to presence of close pores in the samples.

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